(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : 0 467 635 A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number : 91306425.9

(22) Date of filing : 16.07.91

(51) Int. Cl.[5] : F16L 59/14, C08L 5/00, E21B 43/25

(30) Priority : 19.07.90 GB 9015913

(43) Date of publication of application : 22.01.92 Bulletin 92/04

(84) Designated Contracting States : BE DE DK GB NL

(71) Applicant : LAND & MARINE ENGINEERING LIMITED
Port Causeway, Bromborough
Wirral, Merseyside L62 4TG (GB)

(72) Inventor : Willis, David Alexander
11 Field Hay Lane, Willaston, South Wirral, Cheshi
re L64 1TG (GB)
Inventor : Carmichael, Donald
153 Hernehill Road
London, SE24 0AD (GB)

(74) Representative : W.P. Thompson & Co.
Coopers Building, Church Street
Liverpool L1 3AB (GB)

(54) **Thermally insulating compositions and a method of insulating pipeline bundles and pipeline riser caissons.**

(57) A thermally insulating composition comprises an intimate mixture of a polar base fluid and a heteropolysaccharide, which is principally carbohydrate, comprising 2.8-7.5% (calculated as 0-acetyl) 0-acyl groups, 11.6-14.9% glucuronic acid, and the neutral sugars mannose, glucose and rhamnose in the approximate molar ratio 1 :2 :2 wherein the ratio of terminally linked rhamnose to 1,3 linked rhamnose is 1 :2 and the glucose is primarily 1,3 linked.

In the preferred composition the polar base fluid is monoethyleneglycol and the heteropolysaccharide is the Welan gum BIOZAN.

Due to the gels good thermally insulating properties and rheology the gel finds particular use in a method of insulating pipeline bundles and pipeline riser caissons.

EP 0 467 635 A2

providing beneficial thermally insulating properties, compositions of the invention have been found to exhibit useful pseudoplastic properties, making them ideal for use as pipeline insulation since they can be readily pumped to and from the pipeline.

Without wishing to be bound by theory, it is believed that the thermal insulating properties of a mixture of a gelling agent such as the hetero-polysaccharide BIOZAN and a polar base fluid such as, for example, monoethylene glycol derive from their highly viscoelastic nature. That is, the gelled mixtures whilst appearing fluid, are very much solid-like. In other words they are pseudoplastic, and on experiencing shearing forces, "thin".

This insulating Gel is believed to be the inter-reaction of the long chains of the high molecular weight slightly anionic biopolymers derived from organic base material and the base fluid to be gelled. The lateral extensions of the hydrated biopolymer are believed to be spaced so as to entrap and restrain the base fluid molecules, negating substantially all random movement.

At low shear rates within the base fluid, or when static, the biopolymers orientate themselves randomly, sometimes overlapping, thereby creating a very high viscosity. On initiation of "Flow" or high shear within the Gel, the biopolymers respond virtually immediately by aligning themselves in the direction of flow and deforming their laterals such that restraint upon the base fluid molecules is removed.

This behaviour by the biopolymer is repeatable and/or reversible.

The base fluids used should be of a stable molecular type, not subject to further frationation by application of heat within their freezing/boiling point range, and be capable of carrying a molecualr charge adequate to assist full extension of the hydrated biopolymers laterals. Where the latter is not the case it is necessary to introduce the Gel into an environment in which free, positively charged ions exist. Further, in such cases, it is necessary to introduce into the Gel mix a chelating agent in quantities designed such that the ion migration may only proceed for a given period to avoid coalescence.

The Gel should be so designed so that on development of its rheology, and when full viscosity is reached, substantially all convection within the fluid is negated. As addition of the biopolymer converts the base fluid from a Newtonian to a pseudo plastic property, the Gel will at all times remain highly pumpable. In addition, it is inherent within pseudo-plastic fluids that flow within a restricted environment will immediately become laminar and thus the absence of larger quantities of introduced randomly orientated solids, as would be found in a Newtonian Colloidal suspension Gel, results in very low pumping pressure requirements.

In the example given the biopolymer used is generally termed Welan Gum and marketed under the trade name of BIOZAN.

The chelating agent used is commonly available E.T.D.A.

Using this biopolymer, water (salt or fresh) may be gelled by the introduction of up to 1Kg of Biozan per tonne of base fluid. To avoid excessive ion introduction all contact steel should be properly coated or, alternatively, a high level of chelating agent introduced.

With the alternative base fluid of ethylene glycol an equivalent quantity of Biozan may be used but, because of the poor charge level on the glycol molecule, adjacent steel should not be coated. The addition of a chelating agent in the quantity of 200 ppm will ensure migration does not exceed the desired level.

The invention will now be described by way of example only with reference to Examples 1 to 3, a detailed description of methodology and comparative test data.

Example 1

5.71 kg Biozan
1 m^3 monoethylene glycol

Example 2

5.71 kg Biozan
1 m^3 monoethylene glycol
2 kg EDTA (disodium salt)

Example 3

5.71 kg Biozan
1m^3 monoethylene glycol an effective amount of glutaraldehyde

TABLE 3

2 PPB BIOZAN

	Int.	3 Day	9 Day	2 Week	4 Week +UN	4 Week +SH	6 Week +UN	6 Week +SH	8 Week +UN	8 Week +SH	10 Week +UN	10 Week +SH	12 Week +UN	12 Week +SH
600 rpa	90	90	90	92	230	130	230	142	230	140	230	140	230	140
300 rpa	61	60	60	63	140	95	140	97	140	99	140	98	140	98
200 rpa	50	50	52	52	120	75	114	76	116	77	118	76	117	75
100 rpa	35	35	35	37	89	55	85	55	86	55	87	54	86	54
6 rpa	15	15	15	15	30	17	29	17	29	18	28	18	29	18
3 rpa	13	13	13	13	21	15	20	15	21	15	21	15	21	15

2 PPB BIOZAN - 1% TRIS BUFFER

	Int.	3 day	9 day	2 Week	4 Week +UN	4 Week +SH	6 Week +UN	6 Week +SH	8 Week +UN	8 Week +SH	10 Week +UN	10 Week +SH	12 Week +UN	12 Week +SH
600 rpa	90	91	90	94	160	95	210	160	227	156	234	154	234	154
300 rpa	60	60	60	63	100	65	124	102	134	100	138	104	137	105
200 rpa	50	49	50	52	70	55	95	81	104	86	112	90	112	92
100 rpa	35	35	35	36	50	39	65	58	69	58	78	53	79	55
6 rpa	15	15	15	15	18	15	21	17	21	17	26	18	27	18
3 rpa	13	13	13	13	15	14	17	15	17	15	20	15	21	15

+UN -- Unsheared

+SH -- Sheared

TABLE 4 (Contd.)
BIOZAN IN ETHYLENE GLYCOL
EFFECTS OF TEMPERATURE ON VISCOSITIES

EFFECTIVE VISCOSITIES

	BIOZAN CONCENTRATION				
LB/BBL	1.5	1.75	2.0	2.25	2.5
Kg/M3	4.28	5.00	5.71	6.42	7.13
75°F					
1020 sec-1	84	100	113	109	136
510 sec^{-1}	116	124	138	140	166
340 sec-1	132	148	158	162	191
170 sec^{-1}	171	188	216	228	258
10.2 sec-1	800	850	1050	1150	1300
5.1 sec^{-1}	1300	1400	1800	2000	2200
50°F					
1020 sec-1	122	138	-	-	-
510 sec^{-1}	149	168	190	198	208
340 sec-1	170	194	222	222	240
170 sec^{-1}	219	249	288	294	318
10.2 sec-1	951	1050	1260	1350	1450
5.1 sec^{-1}	1500	1700	2000	2200	2400
40°F					
1020 sec-1	128	-	-	-	-
510 sec^{-1}	162	192	208	213	217
340 sec-1	189	219	239	249	263
170 sec^{-1}	246	279	315	330	348
10.2 sec-1	1000	1150	1400	1450	1600
5.1 sec^{-1}	1600	1800	2200	2300	2600

These results are plotted in Figs. 9 to 12, from which the conclusion to be drawn is that as temperature decreases, ethylene glycol viscosified with Biozan will produce increased viscosities. This is especially noted at high shear rates, i.e. at 24°C, (75°F) 5.71 Kg/M^3 produced a viscosity of 138cP at 511 sec^{-1} when cooled to 10°C, (50°F) viscosity increased to 208cP, an increase of 50%. At 5.1sec^{-1} the viscosity increased from 1800 to 2200cP, an increase of only 22%. Similar trends were seen at the other concentrations.

It will be noted from Example 2 that it may be preferred to incorporate a chelating agent into the composition. This is because the compositions show increased viscosity in the presence of metal ions.

The gelled portion of the fluid did not have the appearance of a true chemically cross-linked polymer and was fragile in nature, the fluid returning to a homogeneous state on the application of shear.

11. A method as claimed in claim 8, 9 or 10 in which the base fluid is monoethylene glycol or the heteropolysaccharide is BIOZAN (Biozan is a Registered Trademark of Merk & Co. Inc.).

12. A method as claimed in any of claims 8 to 11 in which a chelating agent is also added in an amount in excess of 100mg per litre of base fluid.

13. A method of insulating a fluid which is transported along a fluid conducting line housed within a carrier pipe, the method comprising pumping into a space formed between the outer surface of the conducting line and the inner surface of the carrier pipe, a mixture of a heteropolysaccharide, which is principally carbohydrate, comprising 2.8-7.5% (calculated an 0-acetyl) 0-acyl groups, 11.6-14.9% glucuronic acid, and the neutral sugars mannose, glucose and rhamnose in the approximate molar ratio 1:2:2, wherein the ratio of terminally linked rhamnose to 1,4 linked rhamnose is 1:2 and the glucose is primarily 1,3 linked, and a base polar liquid.

14. A method as claimed in claim 13 in which the heteropolysaccharide and base polar liquid are mixed, and subjected to a shearing force sufficient to reduce the viscosity of the mixture by a degree sufficient to allow the mixture to be pumped into the space.

15. A pipeline bundle comprising a first pipe located within a second pipe and defining a space therebetween said space being filled with a composition comprising a heteropolysacchardide, which is principally carbohydrate, comprising 2.8-7.5% (calculated as 0-acetyl) 0-acyl groups, 11.6-14.9% glucuronic acid, and the neutral sugars mannose, glucose and rhamnose in the approximate molar ratio 1:2:2, wherein the ratio of terminally linked rhamnose to 1,4 linked rhamnose a 1:2 and the glucose is primarily 1,3 linked and a polar base fluid.

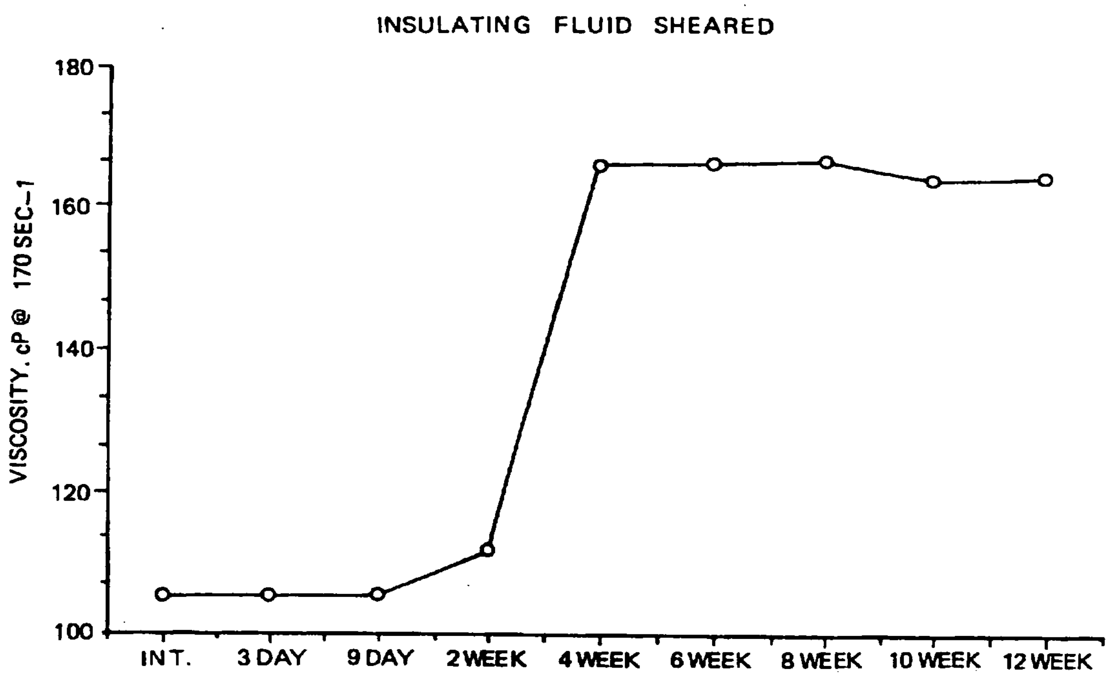

INSULATING FLUID SHEARED
VISCOSITY, cP @ 170 SEC-1
180
160
140
120
100
INT.
3 DAY
9 DAY
2 WEEK
4 WEEK
6 WEEK
8 WEEK
10 WEEK
12 WEEK

FIG. 3

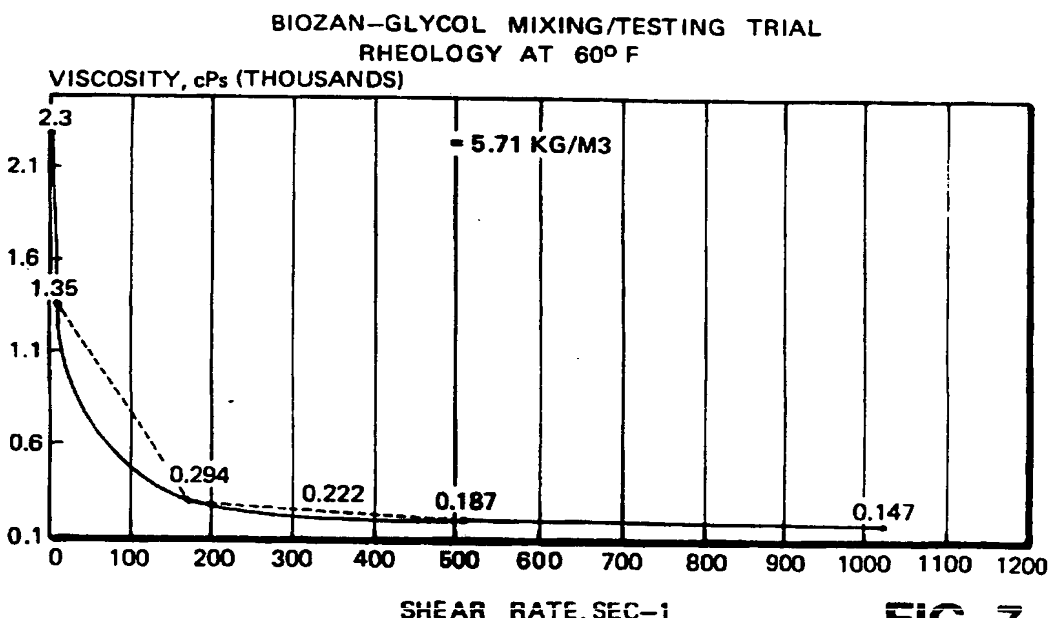
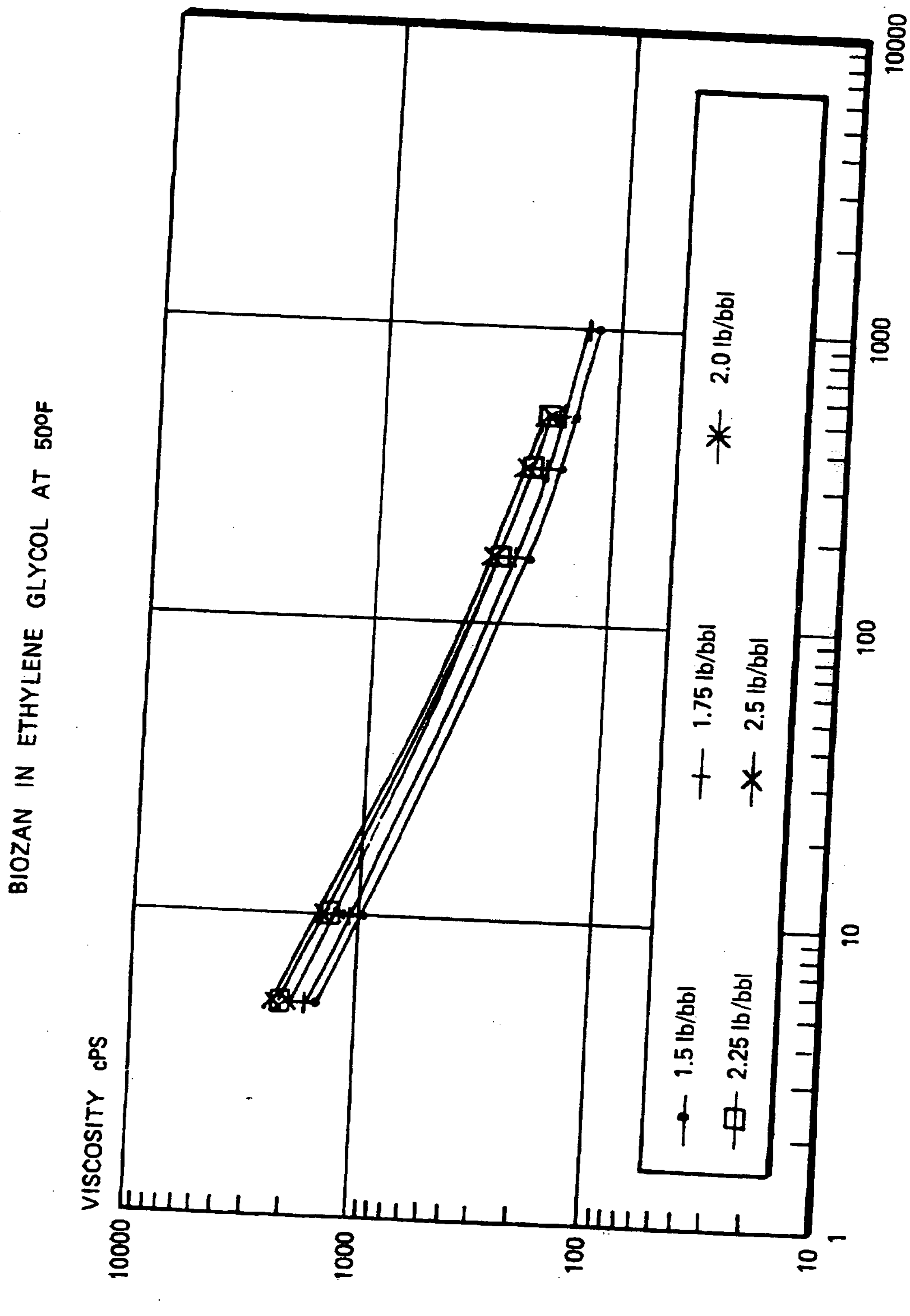

BIOZAN-GLYCOL MIXING/TESTING TRIAL
RHEOLOGY AT 60° F
VISCOSITY, cPs (THOUSANDS)
2.3
2.1
1.6
1.35
1.1
0.6
0.1
= 5.71 KG/M3
0.294
0.222
0.187
0.147
0
100
200
300
400
500
600
700
800
900
1000
1100
1200
SHEAR RATE, SEC-1

FIG. 7



VISCOSITY V. CONCENTRATION

FIG. 11

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number : **0 467 635 A3**

(12) **EUROPEAN PATENT APPLICATION**

(21) Application number : **91306425.9**

(22) Date of filing : **16.07.91**

(51) Int. Cl.[5] : **F16L 59/14**, C08L 5/00, E21B 43/25

(30) Priority : **19.07.90 GB 9015913**

(43) Date of publication of application : **22.01.92 Bulletin 92/04**

(84) Designated Contracting States : **BE DE DK GB NL**

(88) Date of deferred publication of search report : **01.04.92 Bulletin 92/14**

(71) Applicant : **LAND & MARINE ENGINEERING LIMITED**
Port Causeway, Bromborough
Wirral, Merseyside L62 4TG (GB)

(72) Inventor : **Willis, David Alexander**
11 Field Hay Lane, Willaston, South Wirral, Cheshi
re L64 1TG (GB)
Inventor : **Carmichael, Donald**
153 Hernehill Road
London, SE24 0AD (GB)

(74) Representative : **W.P. Thompson & Co.**
Coopers Building, Church Street
Liverpool L1 3AB (GB)

(54) **Thermally insulating compositions and a method of insulating pipeline bundles and pipeline riser caissons.**

(57) A thermally insulating composition comprises an intimate mixture of a polar base fluid and a heteropolysaccharide, which is principally carbohydrate, comprising 2.8-7.5% (calculated as 0-acetyl) 0-acyl groups, 11.6-14.9% glucuronic acid, and the neutral sugars mannose, glucose and rhamnose in the approximate molar ratio 1 :2 :2 wherein the ratio of terminally linked rhamnose to 1,3 linked rhamnose is 1 :2 and the glucose is primarily 1,3 linked.

In the preferred composition the polar base fluid is monoethyleneglycol and the heteropolysaccharide is the Welan gum BIOZAN.

Due to the gels good thermally insulating properties and rheology the gel finds particular use in a method of insulating pipeline bundles and pipeline riser caissons.

EP 0 467 635 A3